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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

γ -Butyrolactone

We, KYOWA CHEMICALS K.K., a Japanese Body Corporate of No 4, 1-chome, Ohte-machi, Chiyoda-ku, Tokyo-to, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 The present invention relates to a process for preparing γ -butyrolactone and a catalyst suitable for use therein.

10 The preparation of γ -butyrolactone by the hydrogenation of maleic anhydride, succinic anhydride, an ester of succinic acid, an ester 15 of maleic acid or an ester of fumaric acid is already known. The hydrogenation may be carried out in the liquid phase using a catalyst preferably a nickel catalyst (e.g. United States Patents Nos 2,772,291 and 2,772,292 20). However this type of hydrogenation requires an elevated temperature and high pressure, and the yields obtained are generally unsatisfactory. It is also possible to carry out the hydrogenation in the vapour phase when the preferred catalyst is copper-chromite.

25 When the hydrogenation is carried out in the liquid phase and on a large scale, a high initial cost is involved and moreover the operation of the process is complicated. Furthermore hitherto known hydrogenation processes in the vapour phase suffer from the disadvantage of having to be carried out at a relatively high temperature, for example, about 300°C, and moreover in order to obtain a good conversion 30 rate, the reaction material should be fed to the catalyst at low speed. It is also difficult to reactivate the copper-chromite catalyst, when the activity has been lowered by use for a period of time.

35 It is an object of the present invention to provide an improved process for the preparation of γ -butyrolactone.

40 According to the present invention, there is provided a process for the preparation of γ -butyrolactone on which maleic anhydride, suc-

cinic anhydride, an ester of maleic acid, an ester of succinic acid or an ester of fumaric acid is hydrogenated in the vapour phase in the presence of a copper-zinc catalyst.

45 Esters which may be hydrogenated according to the process of the present invention include diesters of aliphatic alcohols containing from 1 to 6 carbon atoms.

50 The copper-zinc catalyst used in the process according to the present invention is useful as a catalyst for the preparation of γ -butyrolactone regardless of the proportions of copper and zinc it contains. However, a low ratio of copper to zinc gives a catalyst with low durability, whilst a high ratio of copper to zinc 55 may give rise to a catalyst with a lower activity. It is therefore preferred to use a ratio of zinc to copper within a range of from 95:5 to 1:99 preferably 95:5 to 80:20. It is also possible, if desired, to add small amounts of one or more promoters other than chromium without a serious decrease in the usefulness of the catalyst.

60 The copper-zinc catalyst for use in the process according to the present invention may be prepared either by depositing copper and zinc onto a suitable carrier or by formulation together with an appropriate filler.

65 It is in general possible to prepare the catalyst for use in the process of the present invention by any method, in which the copper and zinc are intimately bonded. It is preferred that the catalyst be prepared by adding an alkali (for example caustic soda, sodium carbonate, etc.) to a solution containing suitable salts of copper and zinc (for example nitrates, sulfates, etc.), washing and drying the resulting precipitate, and effecting reduction with or without the use of a conventional calcination process. It is also possible to prepare the catalyst by 70 mixing a copper-containing compound e.g. copper oxide, copper hydroxide or copper carbonate with a zinc-containing compound e.g. zinc oxide, zinc hydroxide or zinc carbonate, each material having been prepared separately, 75 80 85 90

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mixing with a small quantity of a filler and carrying out calcination and reduction. The reaction may conveniently be carried out at a temperature from 150 to 350°C at atmospheric pressure, or if desired, at a slightly elevated pressure. The reaction is preferably effected in an atmosphere of pure hydrogen gas or a mixture of pure hydrogen gas and a suitable inert gas such as nitrogen.

When maleic anhydride or succinic anhydride is used as a starting material, it is preferred first to dissolve the material in a suitable organic solvent advantageously

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butyrolactone since these substances are solid at room temperature.

The addition of chromium to the copper-zinc catalyst must be avoided. If it is added the reaction temperature will necessarily be required to be higher and the yield obtained will be poor.

The following table shows the adverse effect of the addition of chromium to the copper-zinc catalyst.

In this table, the weight ratio of copper to zinc for the catalyst is 1:1 and the reaction conditions are as follows:—

Starting material	mixture of maleic anhydride and γ -butyrolactone (weight ratio 6:4)
Starting material feed velocity	0.35 g/hr
Molar ratio of hydrogen to maleic anhydride	50:1
Pressure	1 kg/cm ² abs.

Cr/(Cu+Zn+Cr)	Reaction temperature	Yield	
		γ -butyrolactone	succinic anhydride
% w/w	°C	mol %	mol %
0	245	95	1
10	265	86	2
20	280	79	1
50	310	38	2

The major advantage of the present invention is that the copper-zinc catalyst is of high activity and durability. The catalyst exhibits a good activity even at a relatively low temperature, for example, from 200 to 250°C and the starting material may be almost completely converted into γ -butyrolactone even at atmospheric pressure. This is true even when the ratio of starting material to catalyst is high. The catalyst also has a high durability when used for industrial production since the activity of the copper-zinc catalyst decreases only very slowly even when used over very long periods of time.

A further advantage of the catalyst is that when its activity is lowered after prolonged use, it may readily be reactivated by the so-called oxidation and reduction method. It is also possible, if desired, to extract the metals from the spent catalyst by means of a mineral acid. A reactivated catalyst having an activity equal to that of the initial one may then be

obtained for example in a manner similar to that described in the Example given below.

A yet further advantage of the present invention is that the metallic components used for the catalyst i.e. copper and particularly zinc are cheap. The catalyst may be prepared at a lower price than conventional types. This is a particularly desirable feature for industrial processes. The copper-zinc catalysts described above are better than copper-chrome catalysts for the preparation of butyrolactone. The catalytic reaction may be carried out in the vapour phase using a vapourizer. However, it is possible, if desired, to feed at least part of the starting material into the reactor in the liquid phase and to use the heat of reaction for vapourizing the starting material.

The following Examples are given by way of illustration only. The feed velocity of the reaction material is given in terms of the weight of the starting material fed in one hour (regardless of the weight of the solvent, if used)

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5 per unit of weight of copper plus zinc (as metal elements) in the catalyst. The yield is given in mol %, which is expressed as the ratio of the desired product to the starting material used.

The reactions were carried out at atmospheric pressure in all the Examples.

EXAMPLE 1

10 Anhydrous sodium carbonate (245g) was dissolved in water (800 c.c.) with heating and added to a solution, prepared by dissolving dropwise with stirring $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (114g) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (312 g) in water (1.5 litres). When the addition was complete, the solution was stirred and the resulting precipitate was washed with water until the washings were approximately neutral. The precipitate was mixed well with asbestos (233 g) and formed into 5-6mm granules, which were then dried at 110°C overnight to yield 400g of dried catalyst.

15 72 grams of this catalyst (containing 17.8 grams of metallic components and having a weight ratio of copper to zinc of 30:70) were packed in the central portion of a stainless reaction tube having a diameter of 30 mm and a length of 800 mm. The reduction was carried out at 170°-240°C for 6 hours by using a mixture of hydrogen and nitrogen gases (1:4). Butyl maleate was fed through the tube using hydrogen gas in conjunction with a vapouriser at a velocity of 3.6 g/hour. The vapour from the outlet was cooled to condense the reaction product. The mol ratio of the hydrogen to butyl maleate was 70:1. The hydrogenation was carried out at 200°C to give γ -butyrolactone in 94% yield. The yield of butyl succinate was 2% and this could be re-used as starting material for the product of γ -butyrolactone.

EXAMPLE 2

20 A catalyst prepared in a similar manner to that described in Example 1 was used together with a mixture of succinic anhydride and γ -butyrolactone in a weight ratio of 1:1. The hydrogenation was carried out under the following conditions:—

25 Reaction temperature 240°C
Mol ratio of hydrogen to succinic anhydride 70:1
Feed velocity 0.25 g/hr

30 The yields of γ -butyrolactone and unreacted succinic anhydride were 95% and 2% respectively.

EXAMPLE 3

35 A copper-zinc catalyst was prepared in a similar manner to that described in Example 1 with the exception that the nitrates were mixed so as to give a copper-zinc ratio of 70:30. The reduction was carried out at a temperature of from 140 to 210°C for 8 hours. The reaction material was a mixture of maleic anhydride

and γ -butyrolactone in a weight ratio of 1:1. The hydrogenation was carried out under the following conditions:—

40 Reaction temperature 250°C
Mol ratio of hydrogen to maleic anhydride 60:1
Feed velocity 0.27g/hr
The yields of γ -butyrolactone and unreacted succinic anhydride were 94% and 1% respectively.

EXAMPLE 4

45 The catalyst was prepared in a similar manner to that described in Example 3. Butyl succinate was hydrogenated under the following conditions:

50 Reaction temperature 230°C
Mol ratio of hydrogen to succinic anhydride 60:1
Feed velocity 0.20g/hr
The yields of γ -butyrolactone and unreacted butyl succinate were 97% and 1% respectively.

EXAMPLE 5

55 The catalyst was prepared in a similar manner to that described in Example 1 except that the nitrates were mixed to give a copper-zinc weight ratio of 50:50. The reduction was carried out at a temperature of 100°-230°C for 6 hours. The reaction material was a mixture of maleic anhydride and γ -butyrolactone in a weight ratio of 1:1. The hydrogenation was carried out under the following conditions:—

60 Reaction temperature 240°C
Feed velocity 0.30g/hr
Mol ratio of hydrogen to maleic anhydride 70:1

65 The yields of γ -butyrolactone and unreacted succinic anhydride were 95% and 1% respectively.

EXAMPLE 6

70 A copper-zinc catalyst prepared in a similar manner to that described in Example 5 was used to hydrogenate maleic anhydride mixed with γ -butyrolactone (6:4 by weight) under the following conditions:

75 Reaction temperature 265°C
Feed velocity 1.20 g/hr
Mol ratio of hydrogen to maleic anhydride 70:1

80 The yield of γ -butyrolactone was 89% and of succinic acid 7%. The hydrogenation was continued for 300 hours under similar conditions. Meanwhile, the yields of γ -butyrolactone and succinic acid were almost constant.

EXAMPLE 7

85 A copper-zinc catalyst according to Example 3 was used to hydrogenate maleic anhydride mixed with butanol (6:4 by weight) under the following conditions:

Reaction temperature	255°C
Feed velocity	1.00 g/hr
Mol ratio of hydrogen to maleic anhydride	60:1
5 The yield of γ -butyrolactone was 87% and of succinic anhydride 10%.	

EXAMPLE 8
10 Copper-zinc catalysts according to Examples 3 and 5 respectively were compared with the copper chromite catalyst disclosed in Japanese Patent No. 20199/1963 to determine their relative catalytic ability to produce γ -butyrolactone. So that the catalysts used were of

similar shape and dimensional size, the copper chromite catalyst was prepared by pulverizing a commercial copper chromite catalyst, Cu-0203-T 1/8 [available from Harshaw Chemical Co., U.S.A.] and mixing the same with asbestos to form granules having a diameter of about 5-6 mm. The weight ratio of the total of the copper and chromium (as metals) to asbestos was 30:70. The reduction of the copper-chromite catalyst was carried out in a similar manner to that described in the said Japanese Patent No. 20199/1963. The comparison of the three types of the catalyst is shown in the following Tables.

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	A	B	C	D	E	F
I	1:1	0.27	240	60	94	1
III	1:1	0.27	240	60	45	51
	A	B	C	D	E	F
II	1:1	0.30	240	70	95	1
III	1:1	0.30	240	70	88	1

Notes- A — Weight ratio of maleic anhydride to γ -butyrolactone

B — Feed velocity of maleic anhydride per hour and per a unit weight of metals (copper-zinc or copper-chrome)

C — Reaction temperature (C°)

D — Mol ratio of hydrogen to maleic anhydride

E — Yield of γ -butyrolactone (Mol %)

F — Yield of succinic anhydride (Mol %)

I — Catalyst according to Example 3

II — Catalyst according to Example 5

III — Catalyst according to Japanese Patent No. 20199/1963

30 WHAT WE CLAIM IS:—

1. A process for the preparation of γ -butyrolactone in which maleic anhydride, succinic anhydride, an ester of maleic acid, an ester of succinic acid or an ester of fumaric acid is hydrogenated in the vapour phase in the presence of a copper-zinc catalyst.

2. A process as claimed in claim 1 in which the said ester of maleic acid, succinic acid or fumaric acid is a diester of an alcohol containing from 1 to 6 carbon atoms.

3. A process as claimed in claim 1 or claim 2 in which the compound to be hydrogenated is mixed with an organic solvent prior to vapourization.

4. A process as claimed in claim 3 in which the said organic solvent is γ -butyrolactone.

5. A process as claimed in any of claims 1

to 4 in which the reaction is effected at a temperature of from 150 to 350°C.

6. A process as claimed in any of the preceding claims in which the reaction is effected at atmospheric pressure.

7. A process as claimed in any of the preceding claims in which the reaction is effected in an atmosphere of hydrogen gas.

8. A process as claimed in any of claims 1 to 6 in which the reaction is effected in an atmosphere of hydrogen gas diluted with an inert gas.

9. A process as claimed in any of the preceding claims in which the catalyst contains zinc and copper in a weight ratio of from 95:5 to 1:99.

10. A process as claimed in claim 9 in which the said ratio is from 95:5 to 80:20.

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11. A process as claimed in any of the preceding claims in which the catalyst includes a promoter other than chromium.

12. A process as claimed in any of the preceding claims in which the catalyst includes a carrier or filler.

13. A process as claimed in claim 1 substantially as herein described.

14. A process as claimed in claim 1 substantially as herein described in any of the Examples.

15. γ -Butyrolactone when prepared by a process as claimed in any of the preceding claims.

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(54) GAS PHASE HYDROGENATION CATALYST FOR PRODUCING γ -BUTYROLACTONE FROM ANHYDROUS MALEIC ACID, METHOD FOR PREPARING THE SAME AND THE PREPARATION METHOD OF γ -BUTYROLACTONE USING THE SAME CATALYST

(57) Abstract:

PURPOSE: A catalyst suitable for producing γ -butyrolactone from anhydrous maleic acid under mild reaction conditions with high selectivity and yield. γ -butyrolactone, used to prepare solvents such as pyrrolidone or N-methylpyrrolidone and also used as an intermediate to synthesize N-vinylpyrrolidone, polyvinylpyrrolidone, butanediol and tetrahydrofuran, is widely used over various industries, including pesticides, drugs, dyes, petrochemicals and electronic chemicals.

CONSTITUTION: The catalyst is represented by the chemical formula 1, $\text{CuO}(a) \cdot \text{SiO}_2(b) \cdot (100-x)M(x)$, where M is one or more oxides selected from Re, Ag, Sn, N, K, Mg and Ca; 'a' is an integer of 20 to 99; 'b' is an integer of 1 to 80; and 'x' ranging from 0.001 to 5 represents weight percentage. Further, CuO occupies preferably 50–95wt.% in total weight of CuO and SiO₂. The catalyst is prepared by (i) addition of colloidal silica having a surface area of 100–300m², a hydrogen-ion concentration of pH8–10 in a copper salt solution; (ii) coprecipitation of the mixture solution with an addition of an alkali solution followed by hydrothermal aging; (iii) washing the hydrothermally aged solution with deionized water after filtration, and then drying; (iv) supporting CuO catalyst with the precursor of M (referred in chemical formula 1) in such a manner that M is supported into the CuO catalyst being dissolved in an organic solvent or water. According to the present invention, γ -butyrolactone is manufactured by after activating the present catalyst, supplying a gaseous mixture of anhydrous maleic acid and hydrogen in the presence of the activated catalyst, and then reacting at 220–350deg.C under a pressure of normal pressure to 20atm.

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